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(54) Metallic Pipe Provided with Protection Against Corrosion and a Method for the Production Thereof

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ABSTRACT

A metallic pipe for use, for example, as a brake-line, a fuel-line or a line for motor vehicles, is provided with corrosion-protection against chemical or mechanical attack. The corrosion-protection consists of a plurality of layers, at least one of which layers is made of a metal or metal-alloy.

In order to provide a pipe of this kind with multilayer corrosion-protection, it is necessary to ensure that the individual layers adhere to each other, and that the pipe is sufficiently flexible to withstand a high degree of deformation. To achieve these objectives, a metal-alloy layer consisting of low-melting-point metals, be applied to the outer surface of the pipe. An intermediate layer, both sides of which are adapted to adhere, is applied over the aforementioned metal-alloy layer. At least one layer of a highly-resistant, thermoplastic or thermosetting synthetic material is then formed over the intermediate layer.

The invention relates to a metallic pipe which is provided with corrosion-protection against chemical and/or mechanical attack, the said corrosion-protection consisting of a plurality of layers, at least one of which is a layer made of a metal or a metal-alloy; and to a method for applying the layers.

Metallic, corrosion-protected pipes of this kind are intended to remain corrosion-resistant even after being deformed and, during use, under stress caused by impact, shock and bending. Such properties are needed for motor-vehicle parts, for example. It is known to provide a galvanized part with a chromate coating following a coating on non-wax synthetic material, followed in turn by a heat-treatment. The known method leads to a multilayer protective coating. See for example, German Patent No. 20 46 449 or U.S. Patent No. 3,808,057.

It is also known to apply protective coatings to metal objects using a reducing agent and compounds of aqueous dispersion containing hexavalent chromium, a dispersion being used which is a hydrophobic resin of a non-wax nature, which may be hardenable or thermoplastic, is added. See German Auslegeschrift AS 12 46 357.

In contrast to this, it is the purpose of the present invention to provide a metal object with multilayer corrosion-protection in which mutual adhesion of individual layers is sufficiently flexible to withstand a high degree of deformation, and which exhibits still greater resistance to corrosion.

According to the invention, this purpose is accomplished by first applying a metal-alloy layer, consisting of low-melting-point metals, to the surface to be protected. Next, an intermediate layer, both sides of which are adapted to adhere, is applied over the metal-alloy layer. Then, at least one layer of a highly corrosion-resistant, thermoplastic or thermosetting synthetic material is formed on the intermediate layer. Multilayer corrosion-protection of this kind adheres firmly to the base (the metal surface to be protected), while the individual layers adhere firmly to each other, said layers being extremely flexible and

able to withstand considerable deformation, as in pipe-bending, for example. Another advantage of the protection is its great resistance to base-metal corrosion tests according to DIN 50018/2.0 S (intensified industrial atmosphere) and ASTM-B117 (salt-spray test). This corrosion-protection coating exhibits homogeneous behaviour with appropriate resilient adjustment of its components.

These and other beneficial objects of the invention may be achieved by providing on a metal surface to be protected: a metal layer applied to the surface; an intermediate layer, both sides of which are adapted to adhere, applied over the layer of metal; and at least one layer of a highly resistant, thermoplastic or thermosetting synthetic material formed on the said intermediate layer.

These and other beneficial objects of the invention may also be achieved by providing on a metal surface to be protected: a metal or metal-alloy layer, consisting of low-melting-point metals, applied to the surface; a layer of chromate applied over the metal or metal-alloy layer; an intermediate layer, both sides of which are adapted to adhere, applied over the chromate layer; and at least one layer of a highly resistant, thermoplastic or thermosetting synthetic material is formed on the said intermediate layer.

In view of the different melting ranges and temperatures at which the films are formed, the invention may be carried out in such a manner that, in the case of a metal-alloy layer made of low-melting-point metals, the intermediate layer is applied as a short-term heat-insulating and barrier layer, while the higher-melting-point, highly resistant, thermoplastic or thermosetting synthetic material is applied as the outermost layer.

An important advantage is that the intermediate layer makes it possible to apply high-melting-point synthetic or thermosetting materials, which need higher temperatures to react, to low-melting-point metal alloys. During the application of the synthetic material, there is no liquating of the metal alloy and accumulations of the metal alloy, with the formation of free zones

on the metal object, are avoided. In this case, the intermediate layer acts mainly as a barrier-layer, preventing the metal alloy from coalescing. After the synthetic material has been applied, the intermediate layer effects a particularly intimate union between the synthetic material and the metal alloy. These properties are exhibited by mixed polymers, for example, synthetic resins in which adhesion is also present at high temperatures.

According to one embodiment of the invention, an advantageous metal alloy is a layer of a lead-tin alloy, since this is soft, flexible and economically viable. The use of a lead-tin alloy is also supported by the range of equipment available in this field.

The abovementioned alloy is always effective. However, the best results are obtained when it comprises, for example, 60 parts of lead and 40 parts of zinc. This composition is economical and is also safe and reliable for personnel processing lead. Moreover, it has a relatively low melting point, thus saving power during processing.

In the processing of such low-melting-point alloys, a layer of the metal alloy about 4 to 10 μm in thickness is sufficient to form an initial corrosion-retardant. In practice, a uniform layer of this thickness is easy to apply and withstands subsequent deformation of the metal object.

In another embodiment, a layer of zinc may be applied, which layer desirably consists of galvanically deposited zinc. According to another aspect of the invention, it is desirable that the intermediate layer adhere well to the underlying metal, metal-alloy or chromate layer. Such an intermediate layer ensures the desired adhesion and, at the same time, constitutes a dense, homogeneous surface, with which the desired barrier-effect is associated. Furthermore, in conjunction with the metal or metal alloy, the said intermediate layer is sufficiently elastic to withstand higher degrees of deformation without cracking or even peeling.

The union between the metal alloy and the intermediate layer is substantially promoted if the temperature at which the inter-

mediate-layer film is formed is lower than the melting point of the underlying metal-alloy layer. Such temperature conditions also prevent the metal alloy from coalescing.

With respect to the relationship between the intermediate layer and the layer of synthetic material, it is desirable that the intermediate layer be highly resilient and adhesive, as compared with the layer of synthetic material.

The resistance of the metallic object to corrosion may be increased by arranging additional layers of highly-resistant synthetic material upon the intermediate layer.

According to the invention, the build-up of layers is achieved in the following manner. The metal or metal-alloy layer is applied from the molten phase, mechanically or galvanically, in a continuous operation. The intermediate layer, comprising a primer, is applied by flow-coating or by spraying from a solvent-phase or dispersion-phase or electrostatically from the solid phase.

The synthetic material is applied by flow-coating, by spraying from a solvent-phase or dispersion-phase or electrostatically from the solid phase.

The metal-alloy layer is applied at a temperature of about 190 to 235° C., depending upon operating conditions.

An economical operating process is, therefore, based upon the highly resistant synthetic material being stoved at about 240 to 270°C., being dried and melted onto the underlying intermediate layer.

The method according to the invention is particularly suitable for metal objects in the form of metal pipes, especially pipes made of steel, used for example, as brake-lines, fuel-lines or as hydraulic lines for motor vehicles.

In order that the invention may be readily understood, several embodiments thereof will now be described in detail, by way of example, with reference to the accompanying drawings in which:

Fig. 1 is a cross-section through a pipe with a single coating of synthetic material;

Fig. 2 is a cross-section through a pipe with a double coating

of synthetic material;

Fig. 3 is a cross-section through a pipe with a chromate layer and a single coating of synthetic material;

Fig. 4 is a cross-section through a pipe with a chromate layer and a double coating of synthetic material.

In the exemplary embodiments, the metal object to be protectively coated is a seamless, welded or double-walled rolled pipe. Applied to this pipe is corrosion-protection against chemcial and/or mechanical attack in the form of a plurality of layers. In Fig. 1, a metal-alloy layer 3 is applied conventionally to surface 2 of the pipe, designated by the reference numeral 1, said layer 3 comprising, for example, two low-melting-point metals. Lead and tin are preferably used as the low-melting-point metals in a 60:40 alloying ratio. After layer 3 has solidified, an intermediate layer 5, e.g. a primer, is applied. The intermediate layer 5 consists of a bonding-agent system comprising a synthetic resin and containing, among other things, corrosion-inhibiting fillers. In this case, the intermediate layer 5 acts as an adhesive and is therefore highly adhesive on the side facing metal-alloy layer 3. On the other side, the intermediate layer 5 adheres to a highly resistant, thermoplastic synthetic-material layer 6, which is now applied; as already indicated, this may be replaced by a thermosetting material. Polyvinyl-fluoride (PVF) and polyvinyl-difluoride (PVF2) are particularly suitable.

Metal-alloy layer 3 is about 4 to 10 μm in thickness, thus providing a high-speed process. Intermediate layer 5, i.e. the so-called primer, in the form of a synthetic resin, is such that it adheres firmly to underlying metal-alloy layer 3.

In one particular exemplary embodiment, both intermediate layer 5 and layer 6 of synthetic material are highly resilient, highly adhesive and heat-resistant.

According to Fig. 2, an additional layer 6 of highly resistant synthetic material or highly resistant thermosetting material is provided. The application of an additional layer 6 does not require an additional intermediate layer.

The advantages of the pipe protected, according to the invention, against corrosion will be apparent if the following tests are carried out:

A lead-tin coated steel pipe 1 would not withstand the salt-spray test according to the ASTM-B117, i.e. after about 360 hours such a pipe would exhibit base-metal corrosion (red rust). The test according to DIN 50018/2.0 S (intensified industrial atmosphere) would produce poor results with a lead-tin coated pipe. According to this test, (corresponding to 2 litres of SO_2), only one cycle is completed before base-metal corrosion becomes visible.

A galvanized steel pipe, carrying a layer of chromate and a layer of synthetic material, completes more than 50 cycles according to DIN 50018/2.0 S or more than 5000 hours according to ASTM-B 117 before base-metal corrosion appears.

According to the invention, steel pipes carrying a coating of lead-tin, an intermediate layer and a layer of synthetic material also complete more than 50 cycles according to DIN 50018/2.0 S or 5000 hours according to ASTM-B 117.

According to the invention, steel pipes carrying a coating of zinc, an intermediate layer and a layer of synthetic material complete more than 60 cycles according to DIN 50018/2.0 S or 7,500 hours according to ASTM-B 117.

According to Fig. 3 or 4, it is also possible to apply a layer 4 of chromate between metal or metal-alloy layer 3 and intermediate layer 5 which has a positive effect upon resistance to corrosion in that it prevents sub-migration, such as may arise in the event of damage (flying stones).

It will be understood that the invention is not limited to the exact constructions shown and described, but that various changes and modifications may be made without departing from the spirit and scope of the invention as defined in the appended claims.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A metallic pipe having corrosion protection applied to a surface of the object, said protection comprising a first layer of a metal or of a metal-alloy of low-melting-point metals overlying the surface and in contact therewith, an intermediate layer, both sides of which are adapted to adhere, overlying the first layer and in contact therewith; and at least one layer of a highly resistant, thermoplastic or thermosetting synthetic material is formed on said intermediate layer.

2. A metallic pipe having corrosion protection applied to a surface of the pipe, said protection comprising a first metal layer overlying the surface and in contact therewith; an intermediate layer, both sides of which are adapted to adhere, overlying the first metal layer and in contact therewith; and at least one layer of a highly resistant, thermoplastic or thermosetting synthetic material is formed on said intermediate layer.

3. A metallic pipe having corrosion protection applied to a surface of the pipe, said protection comprising a first layer of a metal or of a metal alloy of low-melting-point metals, overlying the surface and in contact therewith; a chromate layer overlying the first layer and in contact therewith; an intermediate layer, both sides of which are adapted to adhere, overlying said chromate layer and in contact therewith; and at least one layer of a highly resistant, thermoplastic or thermosetting synthetic material formed on said intermediate layer.

4. A metallic pipe having corrosion protection applied to a surface of the pipe, said protection comprising a first layer of a metal alloy of low-melting-point metals overlying the surface, an intermediate short-term, heat-insulating and barrier layer overlying the first layer; and a layer of higher-melting-point, highly resistant, thermoplastic or thermosetting synthetic material overlying the intermediate layer.

5. A metal pipe according to claims 1, 3 or 4 wherein the first layer consists of a lead-tin alloy.

6. A metal object according to claim 1, 3 or 4, wherein the first layer consists of a lead-tin alloy composed of 60 parts of lead and 40 parts of tin.

7. A metallic object according to claims 1, 2, or 3, wherein the first layer is between 4 and 10 µm thick.

8. A metallic pipe according to claim 2, wherein the first layer consists of zinc.

9. A metallic pipe according to claims 2, or 8, wherein the first layer consists of a galvanically deposited layer of zinc.

10. A metallic pipe according to claims 1, 2, or 3, wherein the intermediate layer adheres firmly to the first layer, or to the chromate layer located thereunder.

11. A metallic pipe according to claims 1, 2, or 3, characterized in that the temperature at which the film of intermediate layer is formed is lower than the melting point of the first layer positioned thereunder.

12. A metallic pipe according to claims 1, 2, or 3, characterized in that the intermediate layer has high resilient and adhesive properties.

13. A metallic pipe according to claims 1, 2, or 3, wherein additional layers of a highly resistant synthetic material are arranged upon the intermediate layer.

14. A method for coating a surface of a metallic pipe so as to impart corrosion resistance thereto, said method comprising:

mechanically or galvanically applying to the surface in a continuous operation a first layer of metal or of a metal alloy of low-melting point metals in the molten phase;

applying an intermediate layer of a primer in a solvent phase or in a dispersion phase over the first layer by flow coating or by spraying; and,

applying a layer of highly resistant thermoplastic or thermosetting synthetic material in a solvent phase or a dispersion phase over the intermediate layer by flow coating or by spraying.

15. A method for coating a surface of a metallic pipe so as to impart corrosion resistance thereto, said method comprising:

mechanically or galvanically applying to the surface in a continuous operation a first layer of metal or of a metal alloy of low-melting point metals in the molten phase;

electrostatically applying an intermediate layer of a primer in the solvent phase over the first layer; and,

applying a layer of highly resistant thermoplastic or thermosetting synthetic material in a solvent phase or a dispersion phase over the intermediate layer by flow coating or by spraying.

16. A method for coating a surface of a metallic pipe so as to impart corrosion resistance thereto, said method comprising:

mechanically or galvanically applying to the surface in a continuous operation a first layer of metal or of a metal alloy of low-melting point metals in the molten phase;

applying an intermediate layer of a primer in a solvent phase or in a dispersion phase over the first layer by flow coating or by spraying; and

electrostatically applying a layer of highly resistant thermoplastic or thermosetting synthetic material in the solid phase over the intermediate layer.

17. A method according to claims 14, 15 or 16, wherein the first layer is applied at a temperature of between 190-235°C.

18. A method according to claims 14, 15 or 16, wherein the highly resistant synthetic material is stoved at a temperature of approximately 240-270°C, wherein it is fused onto the intermediate layer.

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Fig.1

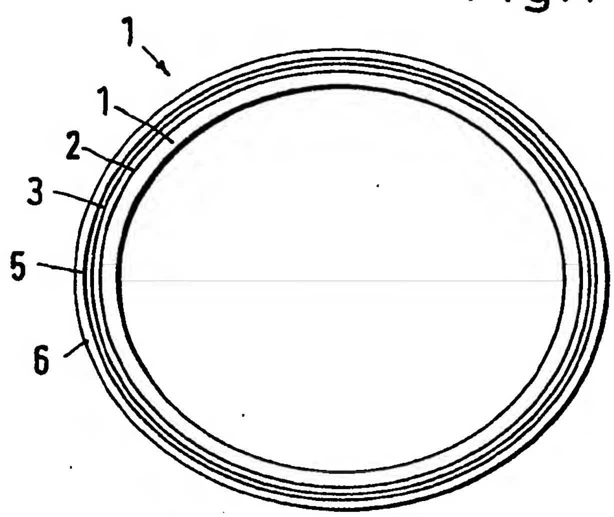

Fig.2

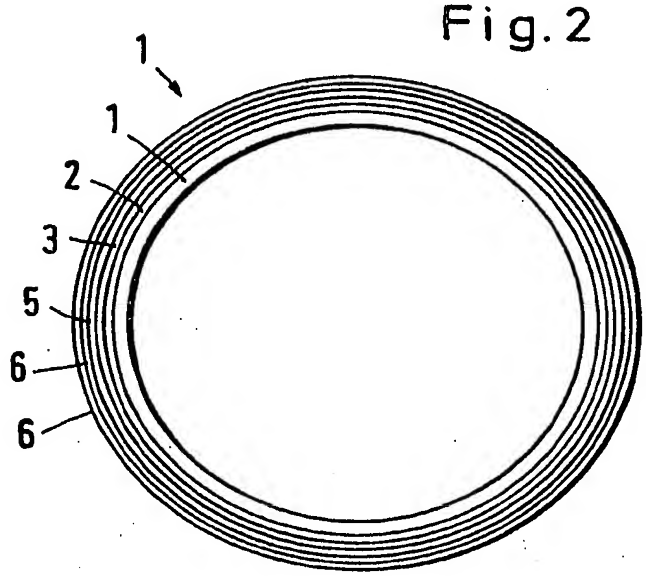

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Fig. 3

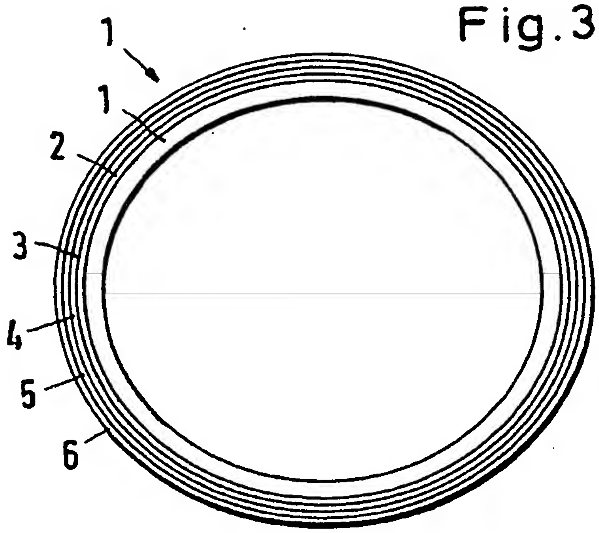
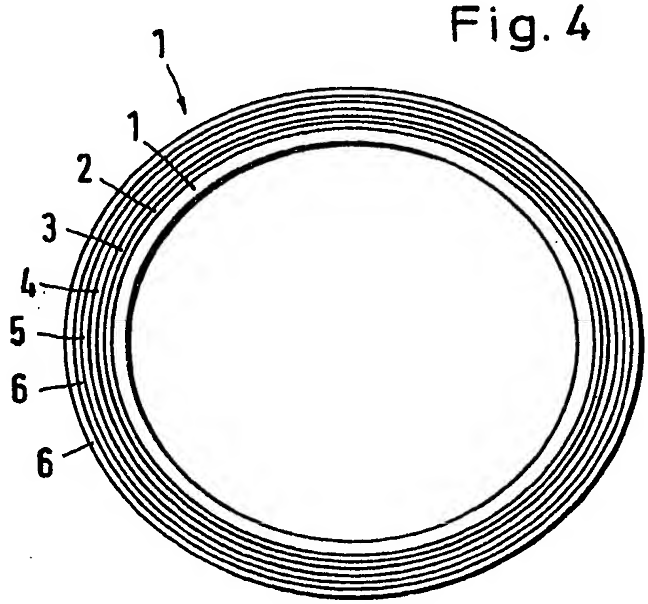


Fig. 4



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